PHYSICAL CHEMISTRY 2012

[11th] International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

ISBN 978-86-82475-27-9 ***Volume*** **1**
ISBN 978-86-82475-28-6 ***Volume*** **II**

Title: PHYSICAL CHEMISTRY 2012 (Proceedings)
Editors: S. Anić and Ž. Čupić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 497; **Format**: B5; Printing finished in September 2012.

Text and Layout: "Jovan"

200- *Coppy printing*

CONTENTS

H-15-P

OPTICAL PROPERTIES OF $ZnO/ZnWO_4$ COMPOSITE NANOPARTICLES

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Abstract
$ZnO/ZnWO_4$ composite rod-like nanoparticles were synthesized by low-temperature soft solution method at 95º C with different reaction times (1-120 hours), in the presence of non-ionic copolymer surfactant Pluronic F68. Optical properties such as reflection and room temperature photoluminescence of obtained samples showed strong dependence on their crystallinity and composition.

Introduction
It is well known that ZnO shows good photocatalytic effect and high quantum activity for degradation of environmental polutants. ZnO has been characterized with its wide bandgap (3.37 eV) and relatively large exciton binding energy (60 meV) at room temperature [1]. $ZnWO_4$ has been also used for water splitting and mineralization of organic pollutants under UV irradiation [2]. Its commercial application is modest because the photocatalytic activity of $ZnWO_4$ is not high enough for the requirements of practical application. Literature data regarding band gap energy are different: ranging from 3.8 - 4.6 eV [3].

The subject of this paper is detailed correlation between structure and morphology of $ZnO/ZnWO_4$ composite nanoparticles and their optical properties. We will show that close junction between ZnO and $ZnWO_4$ and charge transfer processes define optical properties of nanocomposite

Experimental
All chemicals: Na_2WO_4 x $2H_2O$ (99% Riedel-de Haën), $ZnCl_2$ (99% Merck), non-ionic copolymer surfactant Pluronic F68 (Polyoxyethylene-polyoxypropylene block copolymer, M_n~8400 (Aldrich)), NaOH (98% Fluka) and ZnO (≥ 99% Sigma-Aldrich), were of the highest purity available and they were used without further purification. Water employed throughout the work was purified by a Milli-Q system (Millipore) and had a resistivity ≥ 18 MΩ cm^{-1}.

Synthesis of $ZnO/ZnWO_4$ nanoparticles: 0.1 M $ZnCl_2$ solution was mixed with 100 ml of copolymer solution (10 g/L). The pH of the solution was adjusted to 8 using 0.1 M NaOH. Under vigorous stirring, 0.1 M Na_2WO_4 x $2H_2O$ was added drop by drop, and the mixture was refluxed at 95 ^{0}C for 1, 5, 48 and 120 hours, assigned as samples A, B, C, D respectively. During the reflux, precipitation of ZnO and $ZnWO_4$ took place. The obtained $ZnO/ZnWO_4$ nanoparticles were separated from solvent containing copolymer immediately after synthesis by using ultra-centrifugation. Synthesized $ZnO/ZnWO_4$ nanoparticles were washed several times with ethanol and distilled water using centrifugation in every washing step

and annealed at 95 ^{0}C for 18 hours. XRD measurements of obtained powders were used for characterization: samples were mainly $ZnWO_4$ with traces of ZnO [3].

Diffuse reflectance spectra (DRS) of the ZnO/$ZnWO_4$ pellets were recorded using Perkin Elmer Lambda 9 UV-VIS-NIR Spectrophotometer. Photoluminescence (PL) spectra were obtained using Perkin Elmer LS 45 Luminescence spectrometer.

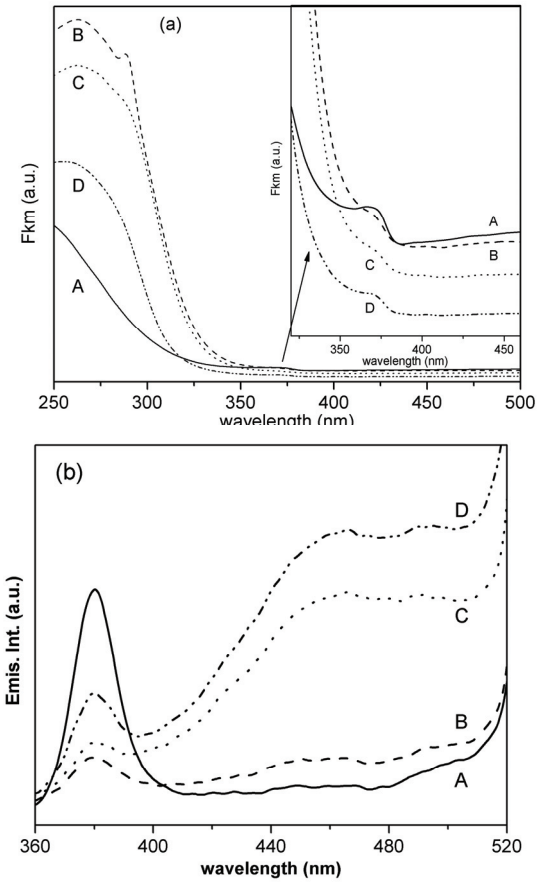

Figure 1. (a) Absorption spectra of obtained powders, calculated from DRS (Kubelka-Munk); (b) PL spectra of obtained powders, λ_{exc}= 270 nm.

Results and Discussion

Optical properties of obtained samples were investigated by diffuse reflectance spectroscopy. Obtained data were converted in absorption units (Fkm) using Kubelka-Munk equation and presented in Figure 1 (a). Two regions of the wavelengths can be observed, region which cover ZnO (~ 3.37 eV) absorption, $\lambda \geq 350$ nm, and region that corresponds to band gap of both ZnO and $ZnWO_4$ (≥ 3.8 eV), $\lambda \leq 350$ nm. The part of the spectra that corresponds to ZnO is enlarged in the inset of Figure 1 (a). As can be seen, sample A shows only one shoulder at about 370 nm, which corresponds well with band gap of ZnO. After that shoulder, absorption increases monotonically with decreasing wavelengths. Most probably in sample A $ZnWO_4$ phase was not formed yet. According to chemical reactions that lead to precipitation of ZnO/$ZnWO_4$ [3], ZnO phase is formed before $ZnWO_4$. In spectra of samples B, D and C a shoulder at the same position (Figure 1 (a), inset, ~ 370 nm) only less stressed, and broad peak at about 270 nm can be seen. This broad peak can be assigned to superposition of ZnO and $ZnWO_4$ absorptions, although its maximum corresponds well with literature data for band gap of $ZnWO_4$ (≤ 4.6 eV). Sample D showed the lowest intensity of absorption in the region of ZnO absorption, probably because ZnO phase is mostly spent on the $ZnWO_4$ synthesis. We presumed that sample A is mainly ZnO and sample D is mainly $ZnWO_4$ with traces of ZnO which can be also detected due to its PL properties.

In PL spectra of all samples, Fig. 1 (b), peak at about 380 nm can be observed with max intensity for sample A and minimum intensity for sample B. This peak can be assigned to ZnO band edge emission. Prolonging synthesis time from 5 h (B), 48 h (C) to 120 h (D) induced increase of intensity of 380 nm peak as well as green emission intensity ($\lambda \geq 400$ nm). These results indicated that prolonged reaction time gives rise to formation of near-surface oxygen vacancies in ZnO which cannot be blocked by formation of $ZnWO_4$ layer. Similar PL spectra measured Kim et al [4] when nanorod arrays of ZnO were surface covered by different oxides (TiO_2, Y_2O_3, CeO_2, and Er_2O_3). Obviously surface layer of $ZnWO_4$ favorably induced the formation of oxygen vacancies in ZnO nanoparticles responsible for green emission. Nanostructured ZnO (Fig. 1 (b) curve A) showed only band edge emission that is typical for small ZnO clusters. This effect can be explained by core/shell structure of composite nanoparticles, where ZnO is core and $ZnWO_4$ exist as a shell which partially cover the surface of ZnO. Figure 2 depicts energetic positions of the conduction and valence bands (cb, vb) of ZnO and $ZnWO_4$ [5]. So, after excitation, all photogenerated holes and electrons are transferred to ZnO part of the composite due to their band edge positions. All observed PL properties originate from ZnO part of the composite.

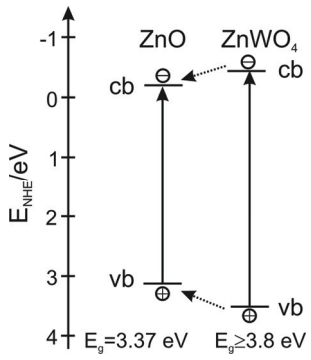

Figure 2. Electronic correlation diagram of the $ZnO/ZnWO_4$ core-shell nanoparticles.

Conclusions

A low temperature method which involves non-ionic copolymer surfactant was used for preparation of $ZnO/ZnWO_4$ composite nanoparticles. The development of ZnO and $ZnWO_4$ phases was followed by optical absorption measurements. Room-temperature PL was observed for all samples (λ_{exc}= 270nm). PL spectra were characterized by band edge emission of ZnO (380 nm) and green emission from oxygen vacancies present in ZnO. Optical properties were correlated and explained by conduction and valence band positions in our composite nanoparticles.

Acknowledgment

Financial support for this study was granted by Ministry of Education and Science of the Republic of Serbia, project 172056.

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CIP Volume I

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

544(082)
621.35(082)
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i primenjene fizičke hemije (11 ; 2012 ; Beograd)
Physical Chemistry 2012 : proceedings. #Vol. #1 / 11th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 24-28, 2012, Belgrade ; [editors S.[Slobodan] Anić and Ž.[Željko] Čupić ; organized by Society of Physical Chemists of Serbia ... et al.]. - Belgrade : Society of Physical Chemists of Serbia, 2012 (Belgrade : Jovan). - VI, 498 str. : ilustr. ; 24 cm

"The Conference is dedicated to Professor Ivan Draganić" --> nasl. str. - Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-27-9
1. Društvo fizikohemičara Srbije (Beograd)
a) Физичка хемија - Зборници b) Електрохемијско инжењерство - Зборници c) Наука о материјалима - Зборници
COBISS.SR-ID 193432332